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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 06/10/2004		3. REPORT TYPE AND DATES COVERED Final 06/10/2004 FINAL REPORT 21 Aug 02 - 31 Dec 03	
4. TITLE AND SUBTITLE New Hierarchically Structured Optical Materials for Dynamic Refractive Index Changes				5. FUNDING NUMBERS Contract# F49620-02-C-0090	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) SBA Materials, Inc. 107 S. La Patera Ln Goleta, CA 93117				8. PERFORMING ORGANIZATION REPORT NUMBER SBA_Final_Report_AFOSR-02-04	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) USAF, AFRL AF Office of Scientific Research 4015 Wilson BLVD Room 713 Arlington VA 22203 NL				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES DD Form 882 Invention Disclosure Filed					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited					12. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 Words) The objective of this proposal was to develop novel materials and devices with dynamically variable refractive index properties, based on new hierarchically ordered composites and porous solids. The dominant innovation is the development of biologically inspired self-assembling inorganic/organic materials, whose versatile response properties can be designed and controlled, according to a variety of specific conditions, field stimuli, and performance criteria. Specifically, it was our goal to create mesostructured composite lens materials with large and reversible changes in their refractive indices ( $\Delta n$ values of 0.5-1.0). This was to be demonstrated, by incorporating components with strong charge-transfer responses to applied optical (near-UV and near-IR) and electrical fields. Modest refractive index changes were obtained in thin film preparations of hybrid mesostructured materials ( $\Delta n$ values of 0.1-0.27). However, we were unable to achieve $\Delta n$ values close to or above 1.0 for isotropic light.					
14. SUBJECT TERMS					15. NUMBER OF PAGES
					16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT					

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**Figure 7:** Above is a typical reflectance spectrum of a photochromic oxazine dye-doped mesostructured thin film. The film was approximately 900 nm thick and homogeneous across the entire 3 cm substrate. Blue line represents ground state and the red line the UV excited state. The  $\Delta n$  of this sample was 0.1.

## Summary

The objective of this proposal was to develop novel materials and devices with dynamically variable refractive index properties, based on new hierarchically ordered composites and porous solids. The dominant innovation is the development of biologically inspired self-assembling inorganic/organic materials, whose versatile response properties can be designed and controlled, according to a variety of specific conditions, field stimuli, and performance criteria. Specifically, it was our goal to create mesostructured composite lens materials with large and reversible changes in their refractive indices ( $\Delta n$  values of 0.5-1.0). This was to be demonstrated, by incorporating components with strong charge-transfer responses to applied optical (near-UV and near-IR) and electrical fields. Modest refractive index changes were obtained in thin film preparations of hybrid mesostructured materials ( $\Delta n$  values of 0.1-0.27). However, we were unable to achieve  $\Delta n$  values close to or above 1.0 for isotropic light.

## Introduction

The program was based on advances made over the past decade at the University of California, Santa Barbara (UCSB) in the areas of inorganic-organic composite and inorganic mesoporous materials syntheses by the research groups of Professor Brad Chmelka (Dept. of Chemical Engineering) and Professor Galen Stucky (Dept. of Chemistry); both of whom were among the founding scientists of SBA Materials, Inc. Key progress has been made in the development of new processable, self-assembled inorganic/block-copolymer composites and mesoporous solids, referred to as the SBA family of mesostructured materials.<sup>1,2</sup> These proprietary materials can be designed, prepared, and functionalized to modify their optical response properties over a wide range of compositions, structures, and macroscopic morphologies, including as films/membranes, fibers, and monoliths, depending on process and device requirements (US and International Patent Applications PCT/US98/26201, PCT/WO99/37705).<sup>4-10</sup> This presents unprecedented opportunities for control over material and device properties. In particular, this can include combinations of highly dissimilar components (e.g., inorganic and organic), which can be organized and coupled across a large common interface. Such breadths of composition, structure, and function make these heterogeneous multicomponent materials extremely versatile. Several reviews of these and similar materials have recently appeared in the literature.<sup>11</sup>

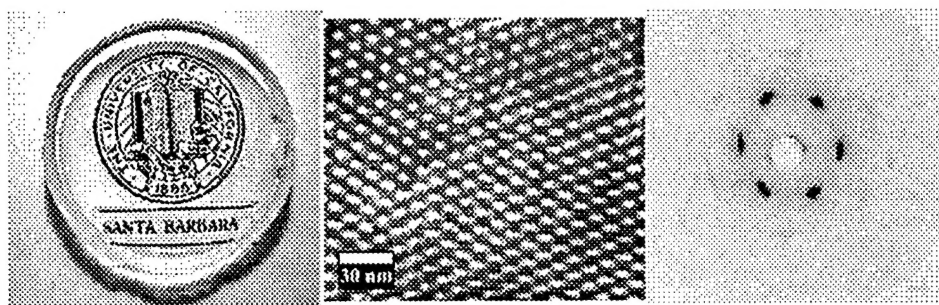
Ordered mesostructured SBA-type materials are synthesized and processed using amphiphilic block copolymers to direct the organization of polymerizing inorganic oxide networks into liquid-crystal-like mesophases.<sup>1,2</sup> The intrinsic processability of the block copolymers allows otherwise intractable ceramics (or other network-forming inorganics, including semiconductors) to be formed into hierarchically ordered structures with separate control over molecular (< 1 nm), mesoscopic (5-50 nm), microscopic (1-20  $\mu$ m), and macroscopic (0.1-10 cm) ordering length scales.<sup>3,14,15,18</sup> The inorganic components subsequently solidify into structures directed by the self-assembling block copolymer species, yielding highly ordered composites that possess increased wall thicknesses compared to other mesostructured material approaches. If desired, these can be converted into ordered mesoporous inorganic solids by extraction or oxidation of the organic components to produce materials with large uniform mesopore sizes (5-30 nm), surface areas exceeding 800 m<sup>2</sup>/g, and mesopore volumes of at least 2.0 cm<sup>3</sup>/g. Among

the important property advantages of SBA-type materials are their unique combinations of optical transparency, optical functionalities, high thermal and mechanical stabilities, compositional and structural diversity, and versatile processabilities into powder, fiber, patterned thin film, or monolith morphologies, including aligned structures.<sup>1,12,13,16-18</sup>

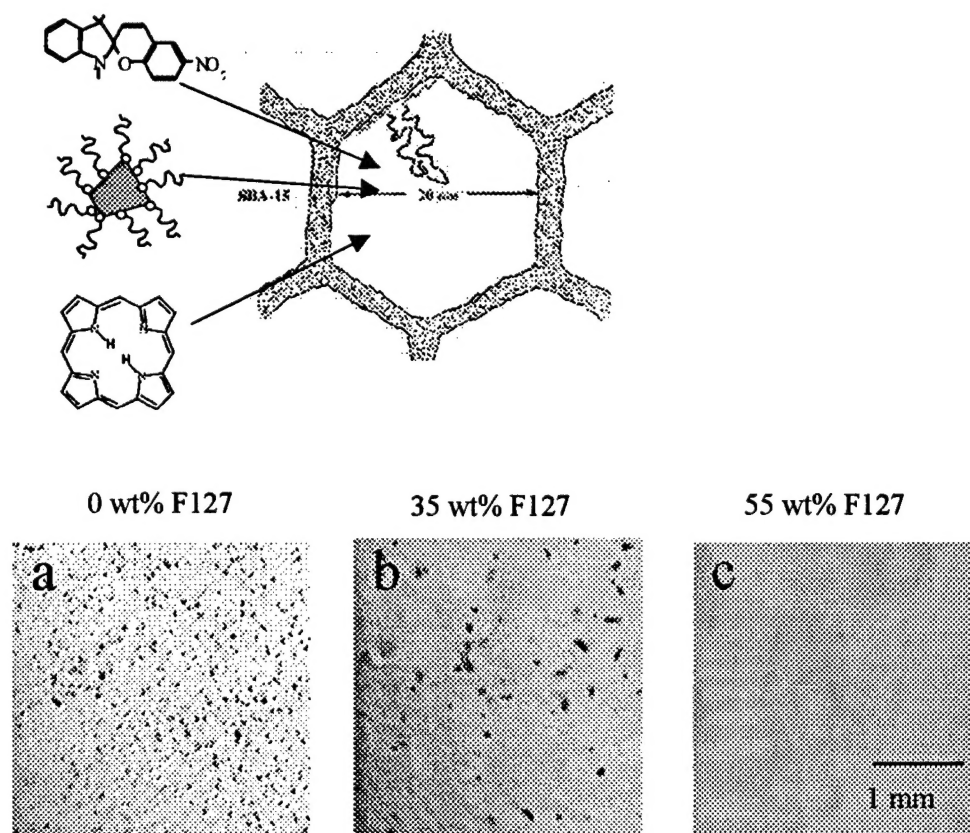
Figure 1 shows an example of the high degree of optical transparency and mesoscopic ordering that can be achieved in SBA-type silica/block copolymer (in this case, amphiphilic polyethyleneoxide-polypropyleneoxide-polyethyleneoxide, PEO-PPO-PEO) monoliths. Such a combination of transparency and mesoscopic ordering in a hybrid inorganic-organic composite provides several advantageous properties that are not possible with systems that are wholly organic or inorganic. The dark regions of the transmission electron micrograph are the silica walls of the inorganic framework, which impart mechanical strength and thermal stability to the material. The light regions are from the hydrophobic PPO component, which nanophase-separates from the hydrophilic PEO block copolymer moieties to provide mesoscopic ordering, alignment, and macroscopic processability. The result is a mesostructured inorganic-organic material that can be molded, cast, printed, and/or polished into a composite lens.

These novel processable, functionalizable, and hierarchically ordered materials can be prepared with a tremendous diversity of compositions and structures to impart tailorable optical properties. This includes the incorporation of organic-soluble optical dyes or surfactant-passivated nanoparticles into the hydrophobic regions of the composites, which allows substantially greater concentrations of the optical agents to be introduced into the materials without macroscopic phase separation. As schematically shown in Figure 2, hydrophobic optical species, such as spiropyrans and porphyrins, or surfactant-passivated nanoparticles are soluble in non-aqueous solvents and are thus readily incorporated into the hydrophobic PPO-rich regions in the transparent mesostructured monoliths. This is clearly shown in Figure 2 for tetraphenylporphyrin dye species incorporated into sol-gel-derived silica monoliths containing different concentrations of PEO-PPO-PEO triblock copolymer. Much higher concentrations of the porphyrin dye are solubilized in the silica/EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub> composite containing 55 wt% of the F127 triblock copolymer species, compared to samples containing lower copolymer weight fractions. From four to ten times higher concentrations of dye species can be introduced into mesostructured silica/PEO-PPO-PEO composites compared to conventional silica glass hosts, providing large improvements in optical sensitivity.<sup>3,19</sup> We have shown for example that this results in substantially lower lasing thresholds (a factor of 20, ref. 3) and significantly greater extents of optical limiting (a factor of five)<sup>19</sup> in mesostructured silica/block copolymer/dye systems that have yet to be optimized. We anticipate still greater sensitivity enhancements to be realized in the near future. Furthermore, the high molecular mobilities within the hydrophobic regions (*e.g.*, PPO) of the composite favor rapid response times, as we have previously demonstrated.<sup>9</sup> The transparent mesoscopically ordered composite materials shown in Figures 1 and 2 thus allow high concentrations of field-responsive species to be introduced into a moldable monolithic lens.

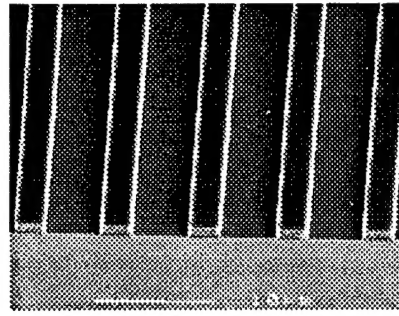
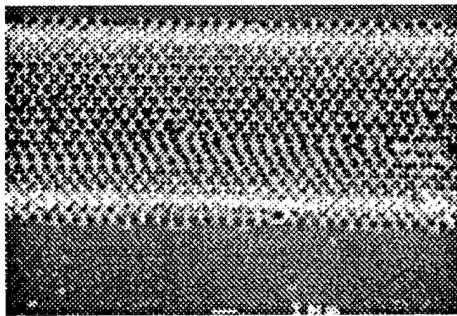
Beyond the incorporation of optical dye species in high concentrations, we were the first to develop the patterning of hierarchically ordered inorganic thin film structures over a



**Figure 1:** A 2.5-cm diameter x 3-mm thick mesostructurally ordered transparent silica/block copolymer monolith prepared with 60 wt% EO<sub>106</sub>-PO<sub>70</sub>-EO<sub>106</sub>. TEM and XRD diffraction results demonstrate the high degrees of mesoscopic and macroscopic orientational ordering in the sample.<sup>12,13</sup>



**Figure 2:** Organic dye species, such as spiropyrans, porphyrins, near-IR chromophores, or surfactant-passivated nanocrystals (also shown), are preferentially incorporated into the hydrophobic regions of the silica/PEO-PPO-PEO composites. These species can be incorporated with higher concentrations and significantly greater homogeneities, as the weight percent of the EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub> (F127) block copolymer species increases.<sup>3,9,19</sup>



**Figure 3:** Optical wave guides hierarchically patterned on both the mesoscopic and photonic length scales by using block-copolymer self-assembly, latex-sphere templating and soft lithography.<sup>3,15,18</sup>



wide range of discrete length scales. Inorganic/block-copolymer self-assembly can be combined with latex-sphere templating and soft-lithography to organize meso/micro/macrosstructured composites and porous solids over independently adjustable 5-50 nm, 0.1-1  $\mu\text{m}$ , 1-10  $\mu\text{m}$  length scales.<sup>15,18</sup> Figure 3 below illustrates the capability of patterning inorganic/organic composites and inorganic porous solids over mesoscopic and photonic dimensions. In addition, we have a great deal of experience with, and in most cases were the first to demonstrate, the inclusion of metal and semiconducting quantum dots, nanocrystals, and nanowires in mesostructured inorganic/block-copolymer composites and porous solids. These include surfactant-passivated capped CdSe quantum dots, titania nanocrystals, and germanium, gold, platinum, silver, or GaAs nanowires in self-assembled inorganic/block-copolymer mesostructures.<sup>2,20-22</sup> We estimate that nanocrystal/nanowire loadings of ~5-80 wt% can be introduced into the composite monoliths, fibers or thin films, with high degrees of mesostructural and orientational ordering. The resulting inorganic-organic SBA-type materials show substantial promise for a variety of different commercial and military applications, including materials with dynamically variable refractive index properties.

## Methods, Assumptions, and Procedures

### Chemicals

Pluronic L64 ( $\text{EO}_{13}\text{PO}_{30}\text{EO}_{13}$ ,  $M_{av}=2900$ , PEO wt%=40%; Aldrich), Pluronic P84 ( $\text{EO}_{19}\text{PO}_{43}\text{EO}_{19}$ ,  $M_{av}=4200$ , PEO wt%=40%; Aldrich), Pluronic P104 ( $\text{EO}_{27}\text{PO}_{61}\text{EO}_{27}$ ,  $M_{av}=5900$ , PEO wt%=40%; Aldrich), Pluronic F88 ( $\text{EO}_{104}\text{PO}_{39}\text{EO}_{104}$ ,  $M_{av}=11400$ , PEO wt%=80%, Aldrich) were gifts from BASF. [1,3-bis(2,3-dihydro-2,2-bis((1-oxohexyl)oxy)methyl)-1H-perimidin-4-yl)-2,4-dihydroxycyclobutene diylum bis(inner salt)]; 1,3,3-Trimethylindolino-6'-bromobenzopyrrolospiran, 1,3,3-Trimethylindolino-6'-nitrobenzopyrrolospiran; 1,3,3-Trimethylindolino-8'-methoxybenzopyrrolospiran; 1,3,3-trimethylindolinobenzopyrrolospiran; 1,3,3-Trimethylindolino-beta-naphthopyrrolospiran; 1,3,3-Trimethylindolino-naphthospirooxazine 1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]oxazine]; 1',3'-Dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]; 1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-phenanthr[9,10-b][1,4]oxazine]; 1',3'-Dihydro-5'-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]; 1',3'-Dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]; 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]oxazine]; 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'[3H]phenanthr[9,10b][1,4]oxazine]; 6-Bromo-1',3'-dihydro-1',3',3'-trimethyl-8-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] were purchased from Aldrich and used without as received. Tetraethyl-orthosilicate (TEOS), methyltriethoxysilane (MTES) were purchased from Gelest. The fluorescence dyes employed in this study were Rhodamine 6G (Molecular Probes) and LD 490 (Exciton).

### Sample Preparation

**Preparation of Dye-Containing Mesostructured Silica / Block Copolymer Composite Monolith** Dye-containing mesostructured silica / block copolymer composite monoliths were prepared in standard 96-well plate through an evaporation-induced self-assembly (EISA) sol-gel processing. A block copolymer was dissolved in a sol of

TEOS/water/ethanol that was pre-hydrolyzed at 60 °C for 2 hours, forming a homogeneous solution, followed by transferring to a standard 96-well plate for gelation of monoliths. In each well, 200 $\mu$ l sol and a concentrated amount of photochromic dye were pipetted. These monoliths were gelled and dried at ambient environment for 3 days and in a 60 °C oven for 1 day.

***Preparation of Dye-Containing Mesostructured Silica / Block Copolymer Composite Thin Films*** Dye-containing (1-15 wt% of initial sol) mesostructured silica/block copolymer composite thin films were prepared using parallel synthesis techniques. Standard multiwell plates were used as reaction vessels to which libraries of various photochromic dyes, silane components, structure directing agents and sol-gel catalysts were added. Silicate precursors were prehydrolyzed for 2 hours in a 60 °C water bath before addition the library. Sols were mixed as follows, solvent (ethanol and or mixtures of various cosolvents), triblock copolymer, photochromic dye and silicate source. Mixtures were stirred and aged for 3h before spin coating. A variety of spin coating parameters were used to create homogeneous high quality films. Typically films were deposited onto a spinning substrate (borosilicate glass or silicon wafers) at 500 rpm for 20 seconds and then accelerated to 1000-4000 rpm for one minute. Samples were allowed to dry overnight in air. Film thickness and refractive indices were measured on a Filmetrics film analyzer.

#### ***Library Design***

Combinatorial compositional monolith and thin film libraries were prepared for high-throughput synthesis and screening for desired dynamic refractive index properties. For the library of each block polymer, the initial polymer mass content was 0%, 1%, 3%, 5%, 7%, 10%, 15% and 20%, and the molar composition was TEOS:HCl(pH=2):ethanol = 1:(4, 8, 12):(4, 12, 20).

#### **Results and Discussion**

One way of the most promising ways to achieve large changes in a material's refractive index,  $n$ , is to introduce components that are sensitive to an optical or electric field and respond by exhibiting a strong change in their electronic charge distribution. In particular, optically responsive species that absorb near-ultraviolet or near-infrared wavelengths are of special interest, because they permit transparency to be maintained in the visible spectrum, while still providing significant charge separation that can lead to large changes in  $n$ . Such species are typically organic molecules (*e.g.*, conjugated systems, polycyclic aromatics, azobenzenes, etc.) which possess electronic structures that produce a large and spontaneous charge redistribution as a result of excitation from their ground states. Such compounds must generally be dispersed in a host matrix to provide the macroscopic properties desired, such as processability, mechanical strength, and optical transparency.

A wide range of photo-stimulable dyes were incorporated into these mesostructured materials. The dielectric constant of such mesostructured materials,  $\epsilon \sim 1.5$ , is much smaller than that of typical inorganic photorefractive crystals,  $\epsilon \sim 30$ . This lower dielectric constant reduces the screening of electrical charges, thereby leading to a greater

stored electric field for the same trapped charge density. As a result, greater changes in optical properties can be realized by choosing appropriate organic components and controlling their orientational ordering within aligned mesostructured materials.<sup>17, 22b</sup>

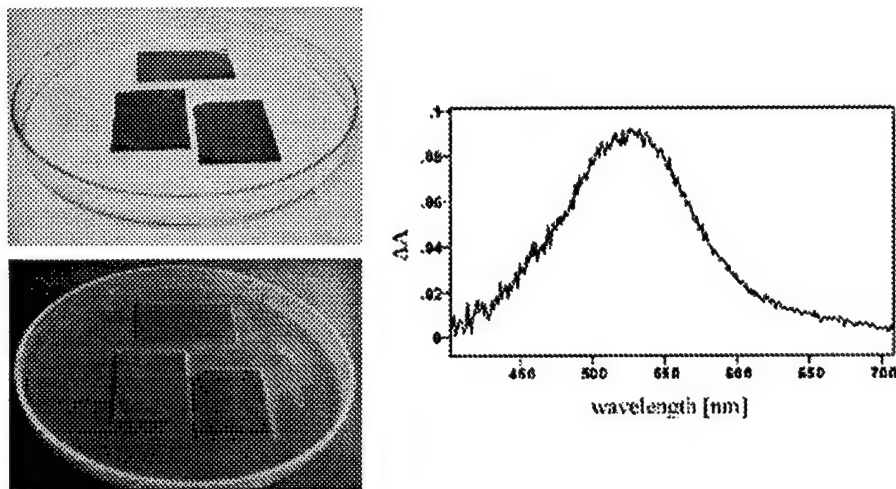
For example, spiropyran dyes are strongly near-UV-absorbing and thermochromic species, which have been introduced into inorganic glass or polymer hosts. We have recently shown that it is advantageous to incorporate spiropyrans and spirooxazines, as well as numerous other organic dye molecules, into mesostructured silica/block-copolymer composites, figure 4.<sup>3,9,19</sup>

Recently, we have demonstrated a substantial photoinduced change in the visible refractive index,  $\Delta n_{avg} = 0.23$ , for a mesostructured thick film composite (1.5 wt% spiropyran/55 wt% EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>/silica) as a result of excitation under longwave (365 nm) UV light. Optically transparent films of these composites were deposited on quartz and silicon substrates and their refractive indices were determined by acquiring multi-wavelength reflectance spectra with an optical analyzer (Filmetrics F20 Analyzer) before and after irradiation with longwave light (365 nm). Figure 4 shows examples of some of the prepared mesostructured dye/composite films along with the difference absorption spectrum for the guest spiropyran thermochrome.

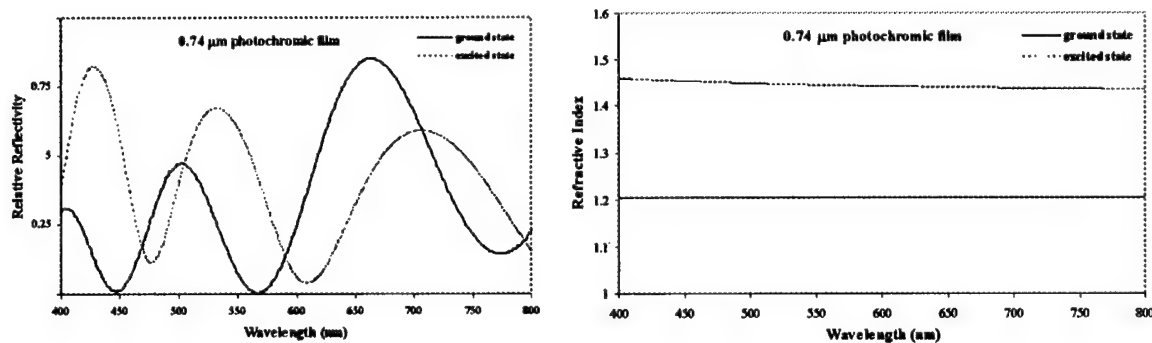
In the course of this program several large hurdles were not surpassed. Films were prepared that could elicit a dynamic refractive index ( $\delta n = 0.1$ -0.27). The change in refractive index was strongly dependent on dye type, concentration and initial solution conditions. In particular they were sensitive to temperature and pH. Many of our films initially have a fairly low pH (around 2) this leads to opening of the spiro ring and in some cases permanently locking the dye into one configuration. In other cases the dyes were transiently providing a substantial  $\delta n$  (0.27) (figure 5) but then would quickly lose that ability (figure 6). There are many possible rearrangements, photochemical and network stabilization pathways that could explain these results. Although we did find a class of spirooxazine dyes that are particular more photochemically stable than the indole dyes in this study.

The desirability of avoiding appreciable absorption in the visible regime means that, in addition to UV-absorbing dyes, agents that absorb at near-infrared wavelengths are also excellent candidates for inducing optically responsive refractive index changes in self-assembled composite lenses. Closely related to the development of near-UV-absorbing large- $\Delta n$  materials, we will similarly incorporate near-infrared (NIR) chromophores, such as cyanines, polyenes, annulenes, and porphyrins,<sup>23</sup> into mesoscopically ordered SBA-type materials. In particular,  $\pi$ -conjugated NIR dyes with low symmetry and strong, separated donor-acceptor moieties often display intramolecular charge migration upon excitation. Analogous to the UV-absorbing spiropyran system described above, NIR-induced charge-transfer leads to changes in the dipole moment of the chromophores,<sup>24</sup> which are manifested as changes in refractive index. Modified donor-acceptor polyenes (e.g., meropolymethines and charged polymethines) and zwitterionic *N*-pyridinium phenolates are particularly promising candidates for displaying near-IR-induced excited-

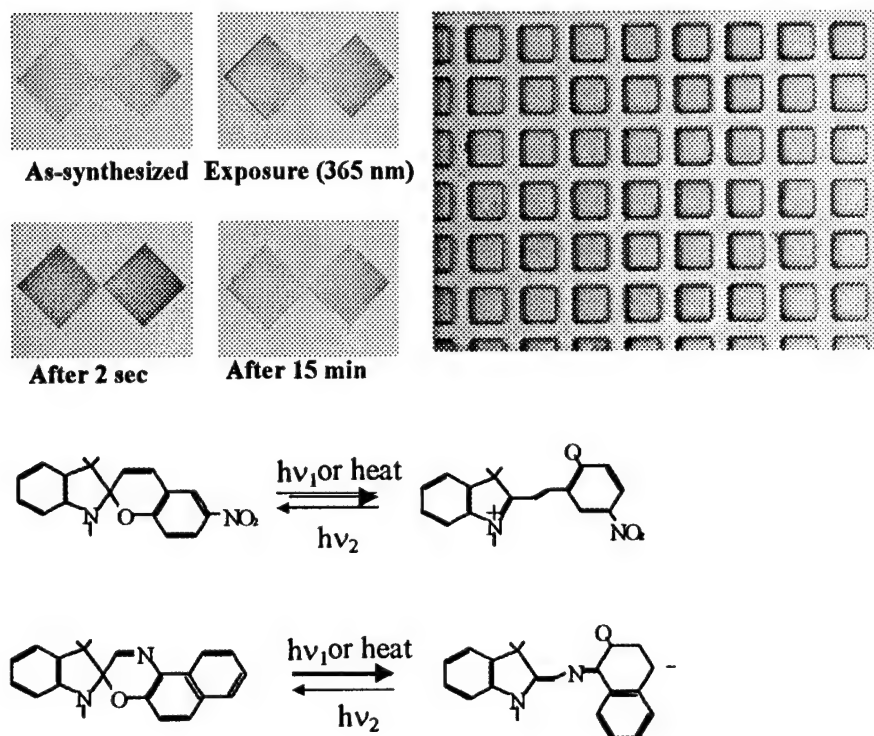
state charge separation<sup>23</sup> with large resultant changes in the refractive indices of bulk EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>/silica/NIR materials. Based on the absorption and charge-transfer



**Figure 4.** Mesostuctured 1- $\mu$ m-thick, silica/EO<sub>106</sub>-PO-70-EO<sub>106</sub> optical films under ambient and longwave irradiation. . The absorption difference spectrum is for the spiropyran dye (1',3'-Dihydro-1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-2(*H*)-indole]) employed here and excited under near-UV light (365 nm).



**Figure 5.** Examples of the observed reflectance spectra and the calculated refractive indices for the mesostructured silica/ $\text{EO}_{106}$ -PO-70- $\text{EO}_{106}$  optical film containing the spiropyran dye in the ground state (blue trace) and excited state (red trace).



**Figure 6:** Different dynamic responses of patterned films of 55 wt%  $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$ -silica composites containing different spiropyran or spiroxazine dye species are shown upon exposure to incident ultraviolet light. Different dye-composite compositions and processing conditions will be explored by using high-throughput synthesis and screening methods, specifically robotic ink-jet printing to deposit systematically varying arrays.<sup>9</sup>

properties of near-IR chromophores, NIR-induced changes in  $\Delta n$  are anticipated to be comparable to those demonstrated for near-UV-absorbing spiropyrans above, with similarly attractive prospects for improvement toward the levels sought by DARPA. Both steady-state (*i.e.*, long-lived, metastable charge separation) and phase-sensitive strategies will be exploited to dynamically vary the bulk refractive indices of these NIR guest/host systems in mesostructured SBA-type films, fibers, and monoliths.

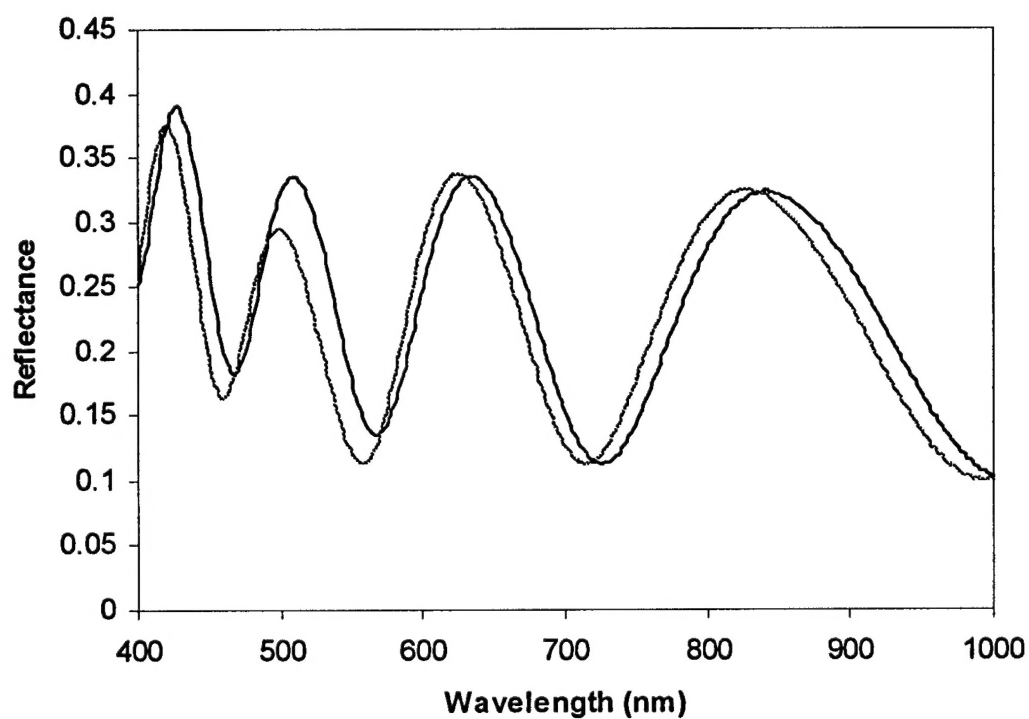
We were able to obtain two very stable NIR dyes from Kodak. The properties of these dyes are proprietary but they have extremely large extinction coefficients. Neither of these dyes were particularly suitable for our chemistry. They had fairly low solubility and aggregated upon concentration. In addition there was no observable large index change upon excitation of the dye.

The demonstration of high concentration dye loadings into both our thin film and monolith form factors was successfully achieved in this program. This was a direct result of our hybrid material properties. The high surface area nanostructure combined with high polymer loadings allowed for a substantial amount of dye to be loaded into our structures, not easily attainable in other sol-gel processes.

There was one particular problem we encountered that has not yet been solved. When thin film structures are made using our chemistry and photochromic materials, the dye is fairly well preserved in the final film. This is what lead to the  $\delta n$  we measured (0.1-0.27). Figure 7 shows a typical reflectance spectrum of a dye-doped mesostructured thin (blue line is ground state) film that exhibits a  $\Delta n$  of 0.1 upon UV excitation (red line). Unfortunately when we tried to transfer that chemistry into functional mesostructured lenses we found that all of the dyes became permanently rendered useless. The chemistry in making lenses and films is not very different at all, but the processing is. When lenses are made over time the concentration of acid grows because of decreasing solvent concentration (due to evaporation). This increasing acid concentration has a detrimental effect on the photochromic dyes in the sol. Their ability to open and close upon photostimulation is destroyed, therefore reducing their ability to dynamically change the refractive index. Although this problem could be solved with the proper development program it did not seem to be solvable in the short time we had left in this program. Unfortunately we had based our initial assumptions on work down with dyes that were acid stable (rhodamine 6G). In these first experiments we demonstrated enhanced laser characteristics of the dye in our mesostructured materials and in addition this is where we first demonstrated ultra high dye loadings. All of these experiments were very successful and lead us to believe that this could be repeated with photochromic dyes. In film form this assumption was true, in monolith form more development is needed.

## Conclusions

The development of mesostructured block-copolymer/silica composite lenses containing near-UV- photochromic species was accomplished to limited degree. As indicated in Figure 2, the hydrophobic dye molecules preferentially associate with the hydrophobic regions of the composites. The resulting dye-containing inorganic-organic mesophases combine many of the otherwise mutually exclusive properties of separate inorganic and



**Figure 7.** Above is a typical reflectance spectrum of a photochromic oxazine dye-doped mesostructured thin film. The film was approximately 900 nm thick and homogeneous across the entire 3 cm substrate. Blue line represents ground state and the red line the UV excited state. The  $\Delta n$  of this sample was 0.1.



polymer host matrices. As a result and as discussed above, the dye species can be introduced homogeneously into the mesostructured composites in much higher concentrations than in inorganic glass matrices alone, providing significantly greater sensitivity and the prospects for substantially higher refractive index changes. Our research group has achieved notable success in producing mesostructured thin films with  $\delta n = 0.1-0.27$ . Unfortunately we were unable to translate this property to a complete monolithic lens. As discussed above there is potential to fix this problem with a proper development program in place.

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